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Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal

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ABSTRACT

In this work, the co-pyrolysis of Indonesian coal (sub-bituminous) and two types of biomass, rice straw and *Leucaena leucocepha* wood, was studied using a drop tube fixed-bed reactor. The gasification reactivity of the obtained co-pyrolyzed char with steam was examined using a rapid heating thermobalance reactor. In the co-pyrolysis, a synergetic effect, in terms of higher gas yield and lower tar and char yields, was manifested especially at a biomass and coal ratio of 1:1. This synergetic effect could be explained by the transferring of active OH and H radicals from the biomass to the coal as well as the catalytic role of potassium (K) from the biomass. In the steam gasification, the *in situ* pyrolyzed char from the coal/biomass blend exhibited a higher reactivity than that from the coal or the biomass. This could be related to the increased surface area and pore volume of chars from the blend as well as the influence of volatile K released from the biomass. In addition, the biomass type appeared to have a significant influence not only on the magnitude of the synergetic effect during the co-pyrolysis but also on the reactivity of the resultant chars.

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1. Introduction

Gasification is a promising technology for producing gaseous fuel ("synthesis gas") from hydrocarbon-based materials. The produced gas can be applied for electricity generation or/and petrochemicals production, such as methanol, dimethyl ether (DME) or/and Fisher–Tropsch processes for producing synthetic fuel oil. Coal, biomass, polymer/plastic and municipal wastes are typical sources used for the gasification processes. At present, coal is the main feedstock used for the gasification process because of its large reserves, and it is expected to be applied as the energy resource for many decades ahead. However, the use of coal has been more concerned because of the environmental impacts that caused from the emission of toxic gases (H_2S, SO_x and NO_x) and the fused-ash slagging problem forming inside the gasifier. In contrast, biomass is a renewable energy resource of interest as a replacement for coal to reduce the environmental impact and fossil fuel usage. Thailand is an agricultural based country with a corresponding large supply of biomass resources. Most such biomass, such as rice straw, rice husk, bagasse, palm oil waste and wood chips, have been utilized for energy purposes, such as combustion and gasification [1]. Unfortunately, gasification of any individual biomass normally encounters several problems such as their seasonal harvesting rather than all year round availability, high transportation costs and lower fuel-qualification characters. Furthermore, the relatively high tar content in most biomass leads to corrosion in the piping and a reduction in the overall gasification efficiency.

The co-utilization of coal and biomass is an interesting way to solve these problems. In recent years, a number of studies have reported a synergetic effect in the co-processing of coal and biomass, in particular co-pyrolysis and co-gasification [2–9]. This synergy during the co-processing is likely to be due to the higher hydrogen and carbon molar ratio (H/C) of biomass compared with coal which could facilitate coal decomposition [2–4,9].

Nevertheless, some studies have reported a lack of any significant synergetic effect when using coal/biomass blends [10–14]. This apparent discrepancy might depend on the operating parameters used, such as temperature, pressure, heating rate, type of reactor, type of coal, type of biomass and biomass blending ratio [2,9,10,15–17]. In a conventional thermobalance reactor, the devolatilization of coal and biomass particles takes place at different time due to the slow heating rate of ~10 °C min^{-1} [13]. The rapid heating rate in a fluidized bed reactor could shorten the time lag of devolatilization but the contact time between the pyrolytic products from coal and biomass is relatively short [14]. This likely explains why no synergetic effect was observed in those studies.

Therefore, in this study the co-pyrolysis of Indonesian sub-bituminous coal and two types of biomass, rice straw (RS) and *Leucaena leucocepha* wood (LN) was carried out in a drop tube fixed-bed reactor. The samples (coal, biomass and coal/biomass blends) were instantly

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Table 1
Proximate and ultimate analysis results of the samples.

Sample	Indonesian coal (Coal)	Rice straw (RS)	*Leucaena leucocepha* (LN)
Proximate analysis (wt.%, as received)			
Moisture	12.41	6.43	8.89
Ash	8.39	11.22	2.59
Volatile matter	36.84	61.95	62.21
Fixed carbon	42.36	29.25	26.31
Ultimate analysis (wt.%, daf)			
Carbon	72.13	45.30	48.39
Hydrogen	6.67	6.93	7.11
Nitrogen	1.4	0.92	0.29
Sulfur[a]	0.22	0.14	0.14
Oxygen (by difference)	19.58	46.71	44.07
H/C molar ratio	1.11	1.84	1.76
O/C molar ratio	0.20	0.77	0.68
Element analysis (wt.%, db)[b]			
Sodium (Na)	0.034	0.064	0.219
Potassium (K)	0.126	1.892	0.823
Calcium (Ca)	0.788	0.844	1.108
Magnesium (Mg)	0.171	0.139	0.186
Silicon (Si)	4.00	11.81	1.00
Iron (Fe)	1.645	0.075	0.165
Gross heating value (kJ/g)	22.66	14.95	12.76

[a] By Bomb washing method (ASTM 3177).
[b] By X-ray fluorescence (XRF).

dropped so that the heating rate of the particles was higher than other typical fixed-bed reactors. The contact time of the pyrolytic products was also presumably longer than that in fluidized-bed reactors, owing to the fixed-bed section. The influence of the biomass blending ratio and biomass type on the product distribution was studied. Their interactions, in terms of the product distribution and gas composition, were described by comparing experiments of coal or biomass alone to coal/biomass blends. The pyrolytic tar and char were characterized with Brunauer–Emmitt–Teller (BET), scanning electron microcopy (SEM) and gas chromatography–mass spectrometry (GC–MS) techniques. In addition, the synergetic effect on the *in situ* char steam gasification rate was investigated using a rapid heating thermobalance reactor.

2. Experimental

2.1. Fuel samples

Indonesian sub-bituminous coal (referred to as coal hereafter), rice straw (RS) and *L. leucocepha* (LN) were ground and sieved into particle sizes of 150–250 μm. To remove the effect of varying moisture contents, the samples were oven-dried at 110 °C for 1 h and then stored in a desiccator before testing. Proximate and elemental analysis results of the samples are shown in Table 1. Coal/biomass blends were prepared by physical mixing at biomass and coal weight ratio of 0:1, 1:3, 1:1, 3:1 and 1:0, respectively.

2.2. Pyrolysis in a drop tube fixed-bed reactor

Pyrolysis of coal, biomass (RS or LN) at the different ratio of coal/biomass blends was performed in a drop tube fixed-bed reactor, as illustrated schematically in Fig. 1. The quartz-tube reactor, which had an inner diameter of 20 mm and a length of 580 mm, was heated externally by a Nabertherm RS 8013001M electric furnace. The heating zone (340 mm length) was located in the middle of the reactor tube. N_2 was used as the carrier gas at a total gas flow rate of 120 mL min^{-1}. After the reactor was heated to 800 °C and held for 1 h, 4 g of sample was instantly dropped into the reactor. The fast pyrolysis immediately took place within the short residence time. The char was produced over a quartz wool filter, which was subsequently weighed for calculating the char yield. Some of the heavy tars were condensed by an iced-tar trap filled with isopropanol and round glass beads of 6 mm in diameter to enhance its capability for recovering condensable compounds.

The chemical structure of the condensed tar was characterized by GC–MS analysis (Section 2.3). The produced gases were collected in a 2-L gas bag and further quantitatively analyzed by GC with a thermal conductivity detector (TCD–GC). The gas collection bag was changed

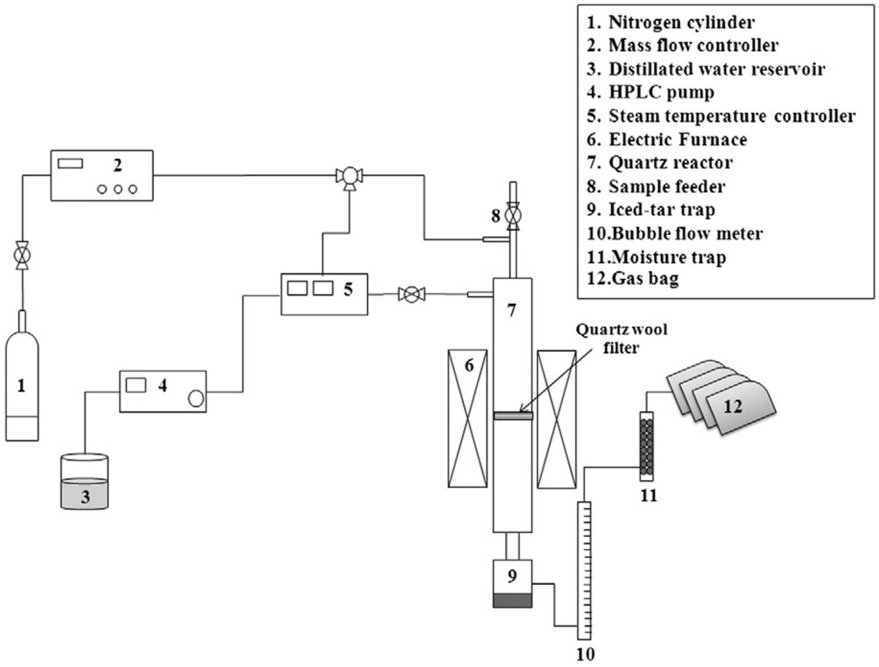


Fig. 1. Schematic image of the drop tube fixed-bed reactor.

every 15 min after the sample was dropped over the 1 h reaction time. For the coal/biomass blends, the calculation yield (Y_{cal}) was obtained by following Eq. (1) to compare with the experimentally derived value.

$$Y_{\mathrm{cal}} = X_{\mathrm{b}} \times Y_{\mathrm{b}} + (1-X_{\mathrm{b}}) \times Y_{\mathrm{c}}, \tag{1}$$

where X_{b} is the mass fraction of biomass in the blend, and Y_{b} and Y_{c} are the individual yield of biomass and coal, respectively.

2.3. Characterization of pyrolytic products

The produced gases (mainly H_2, CO, CH_4 and CO_2) were quantitatively analyzed by TCD–GC (Shimadzu GC-2014) using Ar as carrier gas and a Unibeads C column (3.00 mm I.D. × 2000 mm length). Some of the condensed tar in the ice–tar trap was analyzed to determine the chemical composition by GC–MS on a Varian Model Saturn 2200 equipped with a DB-5 ms capillary column (0.25 mm o.d. × 0.25 mm film thickness × 30 m length, J&W Scientific) using helium as the carrier gas. The molecular weight scan range was 50–650 m/z with a 5 min solvent cut time. The column was held at 50 °C for 3 min, and then the temperature was increased to 220 °C with a heating rate of 20 °C/min and held for 40 min. The pyrolyzed char was analyzed with a CHN analyzer (LECO CHN-2000). The specific surface area, pore volume and pore size of the pyrolyzed chars were measured by N_2 adsorption at −196 °C using the BET method (model Quantachrome, Autosorb-1). Samples were degassed at 300 °C for 6 h before adsorption. The results of physical properties of all pyrolyzed chars were summarized in Table 2. The morphology of the pyrolyzed chars was also characterized by scanning electron microscope method (SEM) on a model JEOL, JSM-5410LV.

2.4. Steam gasification in a rapid heating thermobalance reactor

Steam gasification of the coal, biomass (RS and LN) and coal/biomass blends was carried out in a thermobalance reactor, as shown in Fig. 2. The thermobalance reactor consisted of quartz reactor (25 mm ID outer tube, 13 mm ID inner tube), an infrared gold image furnace and a balance sensor. A ceramic basket with a platinum mesh filter was suspended with the balance sensor. A 10 mg sample was placed into the ceramic basket and initially heated to 115 °C and held at that temperature for 15 min to evaporate the water inside the sample. Then the samples were heated to 800 °C with a rapid heating rate of 33 °C s^{-1} under an Ar inert atmosphere. The rapid pyrolysis of the sample immediately occurred and the pyrolyzed char was produced. After that steam from the steam generator, that was preheated at 200 °C, was introduced into the reactor and steam gasification of the pyrolyzed char took place. The weight loss of the sample was recorded at a 0.4 s time intervals throughout the 80 min reaction time. The overall rate constant (k) of the char steam gasification was calculated from the obtained weight loss data as expressed in Eq. (2),

$$\frac{1}{1-X_{\mathrm{char}}}\frac{dX_{\mathrm{char}}}{dt} = -k \tag{2}$$

where X_{char} is the conversion of char during steam gasification. The conversion was calculated following Eq. (3),

$$X_{\mathrm{char}} = \frac{X-X_{\mathrm{p}}}{1-X_{\mathrm{p}}}, \tag{3}$$

where X and X_{p} are the conversion of sample to volatile at time (t) and the conversion of sample to volatile in pyrolysis, respectively. Note that the steam gasification rate of the char was assumed to obey the first-order kinetics.

3. Results and discussion

3.1. Synergetic effect during co-pyrolysis

The theoretical and experimental product yields from the pyrolysis of the coal/RS and coal/LN blends at 800 °C are shown in Fig. 3a and b, respectively. Closed symbols represent yield of gas, tar and char obtained from each coal/biomass blend and open symbols represent predicted yield calculated by Eq. (1). It revealed that the coal and biomasses gave quite different product yields corresponding to their main chemical components. At the same pyrolysis temperature, biomass gave a higher conversion level into gas and a corresponding slightly and significantly lower yield of tar and char, respectively, than did the coal. This is relevant to their macrostructures where both biomasses are comprised of cellulose, hemicellulose and lignin that are linked together with relatively weak ether linkages (R–O–R). In contrast, coal is composed of dense polycyclic aromatic hydrocarbons (PAHs), which are more strongly bonded and so resistant to heat than that of the ether bond in either of the biomasses [2]. Consequently, the biomass is more easily decomposed to lighter products than the coal.

Furthermore, it was observed that the experimental product yields obtained from the pyrolysis of the coal/biomass blends were somewhat different from predicted values, deviating the most at biomass and coal ratio of 1:1 with higher gas yield and lower char yield

Table 2
The physical properties of the pyrolyzed chars.

Char sample	Coal	RS	LN	RS:coal = 1:1 (w/w)		LN:coal = 1:1 (w/w)	
				Exp.	Cal.[b]	Exp.	Cal.[b]
Ultimate analysis (wt.%, daf)							
Carbon	89.61	35.94	11.87	61.18	62.78	53.22	50.75
Hydrogen	1.79	1.82	0.41	1.67	1.80	1.26	1.10
Nitrogen	0.88	0.70	0.13	0.68	0.79	0.55	0.51
Oxygen + sulfur[a]	7.72	61.54	87.98	36.47	34.63	44.97	47.64
Element analysis (wt.%, db)[c]							
Sodium (Na)	0.10	0.11	0.10	0.16	0.10	0.19	0.10
Potassium (K)	0.55	2.72	1.45	2.31	1.63	1.38	1.00
Calcium (Ca)	3.20	1.85	5.38	1.26	2.53	1.56	4.29
Magnesium (Mg)	0.24	0.25	0.66	0.42	0.24	0.48	0.45
BET surface area (m^2 g^{-1})	233.81	152.09	119.19	250.28	192.95	210.89	176.50
Pore volume (m^3 g^{-1})	0.157	0.129	0.087	0.175	0.143	0.146	0.122
Pore size (A°)	26.85	34.05	29.14	27.99	30.45	27.74	28.00

[a] By difference.
[b] Calculate from the data of pure coal and pure biomass.
[c] By X-ray fluorescence (XRF).

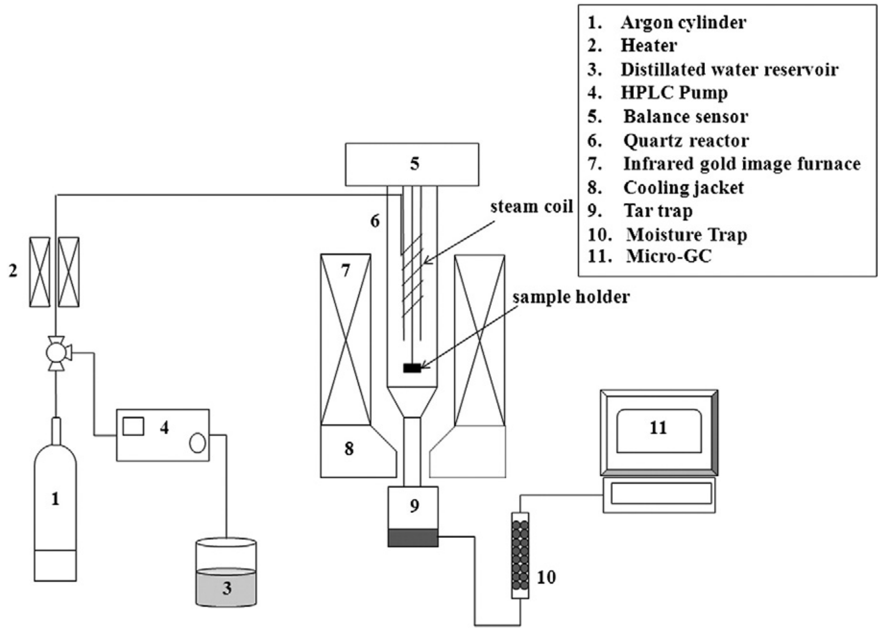


Fig. 2. Schematic image of the thermobalance reactor.

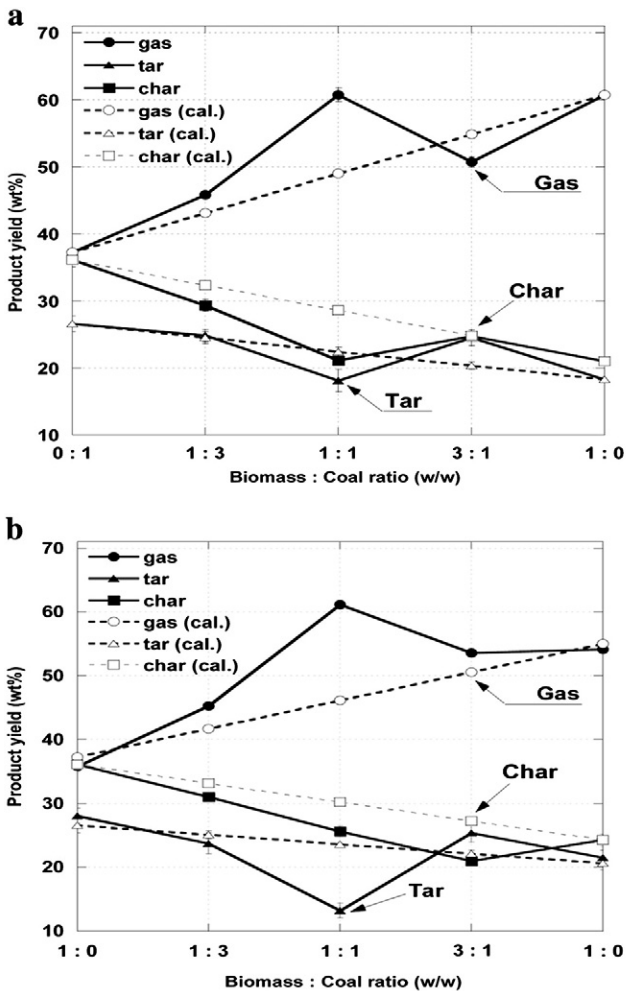


Fig. 3. Experimental and predicted product yields from the pyrolysis in a drop tube fixed-bed reactor at 800 °C of (a) coal with rice straw (RS), and (b) coal with *Leucaena leucocepha* wood (LN), at different coal and biomass ratios (w/w).

than the predicted yields, especially, tar production level. This can be attributed to the fact that the H/C and O/C molar ratios of RS and LN are about 1.8 and 3.4 times higher than those of coal (see Table 1), respectively. Hence, a larger amount of H and OH radicals could be generated and act as hydrogen donor species, promoting the cracking of the aromatic compounds in the coal [2,16]. An explanation for this would be the suppression of secondary reactions, such as condensation, repolymerization and cross-linking reaction, reducing secondary char and tar formation [9,12,18].

As stated above, the synergetic effect was most remarkable at biomass and coal ratio of 1:1 which agrees with the reported co-pyrolysis of lignite and straw in a free fall reactor [2]. It reported that a clear synergy occurred under higher biomass and lignite blending ratios, presumably because the quantity of biomass in the blend provided sufficient hydrogen donors for hydrogenation during the lignite pyrolysis. However, in this study reported here, it was clear that the synergetic effect was reduced or abrogated at a higher biomass and coal ratio of 3:1 (Fig. 3). This is probably due to the production of excess volatiles at high biomass blending system [19].

Additionally, the observed synergetic effect during the co-pyrolysis of coal/RS or coal/LN blends could be attributed to the roles of alkali and alkaline earth metallic species (AAEMs) present in the coal and biomass feedstock. The mineral analysis of the coal and biomass revealed that the biomass contained more AAEM species than coal, especially potassium (K), which was 15.0- and 6.5-fold higher in the RS and LN samples, respectively, than in the coal (Table 1). Potassium has been reported to act as a catalyst for the decomposition of secondary char and char gasification [7,19,20]. In addition, the chars obtained from co-pyrolysis had a larger amount of remaining K than the predicted values, as can be seen in Table 2. It indicates that there would be an essential interaction between K released from biomass and the produced char during the co-pyrolysis of coal and biomass. Kajitani et al. [21] proposed that in the co-pyrolysis of coal with cedar bark, the potassium from the cedar bark was volatilized and then condensed over the coal char surface and so improved its reactivity. The reactivity of char obtained from the coal/biomass blends in steam gasification was also investigated in this study and is discussed in Section 3.3.

The gas produced from the pyrolysis of the different ratio of coal/RS and coal/LN blends at 800 °C revealed that the observed experimental yields of CO were higher than that of the predicted values

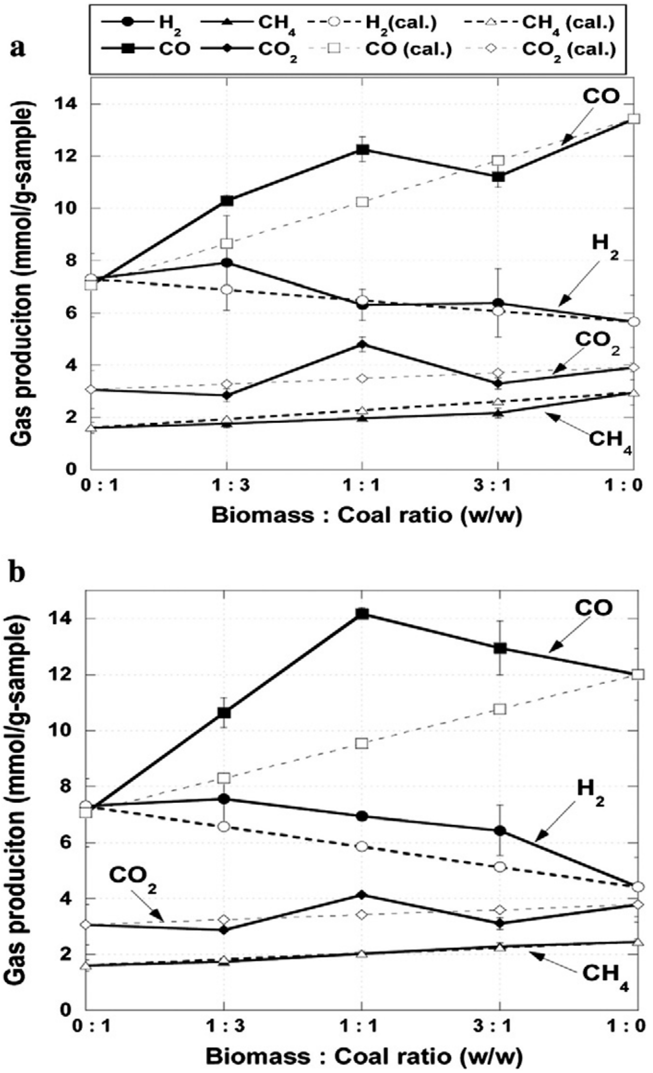


Fig. 4. Experimental and predicted gas production from pyrolysis in a drop tube fixed-bed reactor at 800 °C of (a) coal with rice straw (RS), and (b) coal with *Leucaena leucocepha* wood (LN), at different coal and biomass ratios (w/w).

for the biomass and coal ratio of 1:3 and 1:1 (w/w) (Fig. 4). This could be due to the OH radicals released from both types of biomass. The OH radicals, formed during co-pyrolysis, can attack the aromatic rings in coal and also react with aliphatic species and combine with carbon atoms to form CO [16]. In addition, a slighter experimental yield of H_2 and CO_2 compared to the predicted yields was observed at a RS and coal ratio of 1:3 for H_2 and 1:1 for CO_2. In contrast, no clear synergy was observed for the production of CH_4 because of the relatively low net levels of CH_4 production.

3.2. Effect of biomass type on the synergetic effect

The synergetic effect of co-pyrolysis on the product yield was somewhat different between the coal/RS and coal/LN blends (Fig. 3). The magnitude of the observed synergy in the gas yield for the coal/RS blends was likely to be related to the decrease in the char yield. While, for the coal/LN blends the synergy in gas yield appeared to be commensurate with the decreased tar yields. Accordingly, the interaction between coal and biomass during their co-pyrolysis is related to the biomass type.

As mentioned in Section 3.1, the enhancement of coal decomposition could be attributed to the increase of active OH and H radicals and the AAEM species from the biomass. Since RS and LN have comparable H/C molar ratios (Table 1) and the content of cellulose and hemicelluloses [21,22], the amount of released OH and H radicals from the RS and LN was presumably similar. However, the AAEM content of RS and LN was different, and in particular the K content was 2.3-fold higher in RS than in LN. During pyrolysis, some of the K is released as a volatile (gas phase) and plays a catalytic role in the pyrolysis and gasification [23], while the rest of the K remains in the char (solid phase). The mineral analysis of char revealed that around 43 wt.% of the K remained in the RS-char compared to only ~10 wt.% in the LN-char. This would be due to the relatively high Si content in the RS-char that promotes the absorption of K to form potassium silicate (K_2SiO_3) [24,25]. When considering the same biomass weights, the amount of released (volatile) K from LN was comparable to that of RS (~0.7–1 wt.%), while the retained K in the LN char was lower. Volatile K, with a high enough mobility to be deposited on the coal char surfaces, was speculated to play a significant role in co-pyrolysis through the promotion of both secondary decomposition and gasification of the nascent char with the steam produced during pyrolysis (pyrolytic steam) [26]. Previously, RS has been shown to generate greater amounts of pyrolytic steam compared to LN [21,22], which could account for the notable decrease in the char formation levels seen in the pyrolysis of the coal/RS blends. This phenomenon was also confirmed by the difference in the content of K remaining in the chars obtained from the pyrolysis of both coal/RS and coal/LN blends, as can be seen in Table 2. The char derived from coal/RS pyrolysis had a larger amount of the retained K than the char derived from coal/LN pyrolysis. It is speculated that the interaction between K released from RS and the produced char was more pronounced than that case of coal/LN blend. It would be due to the relatively high Si content in RS-char (Table 1.), as mentioned above.

For LN and coal ratio of 1:1, volatile K presumably existed in a different form due to the difference of the volatile compounds between RS and LN (Fig. 5), and preferential promoted the decomposition of nascent tar, resulting in lower tar yield. Accordingly, the coal/LN blends exhibited a higher experimental yield of CO and H_2 than the predicted value.

3.3. Synergetic effects during co-gasification in a thermobalance reactor

The relative mass over time of the char, derived from the *in situ* pyrolysis of coal, biomass (RS and LN) and coal/biomass blends (biomass and coal ratio of 1:1), during steam gasification at 800 °C is shown in Fig. 6. Note that the initial time (0 s) was defined as the weight change of the raw sample during the initial pyrolysis before the temperature reached 800 °C. The relative mass loss over time of the coal was markedly different from that of the RS or LN. Coal exhibited a marked decrease in relative mass to ~0.4 during the initial pyrolysis, and then gradually decreased during steam gasification to a relative mass of 0.05 at 5000 s. In contrast, the RS and LN both showed a much larger initial weight loss during pyrolysis (95% conversion in pyrolysis, X_p) and were then almost completely lost (nearly 100% of conversion) within 2000 s (RS) or 500 s (LN) of steam gasification. The coal/biomass blends revealed a lower weight decrease than that predicted for both RS and LN. The derived overall rate constants (k) of the *in situ* pyrolyzed char steam gasification, calculated by applying the first-order kinetic equation rate, are shown in Table 3.

The chars obtained from the co-pyrolysis had higher observed experimental overall rate constants (k) than the predicted values. It indicates that the synergetic effect in terms of the char steam gasification rate was observed. Nevertheless, the synergetic effect in terms of char gasification rate has not been found when preparing char in a typical fixed bed or TG reactor with the slow heating rate [10,28]. In this study, a special thermobalance reactor, which can increase temperature with a rapid heating rate (up to 1980 °C min^{-1}), was used. In this case, the thermal behavior of each component overlapped spatially and temporally such that chemical interactions between coal and biomass were

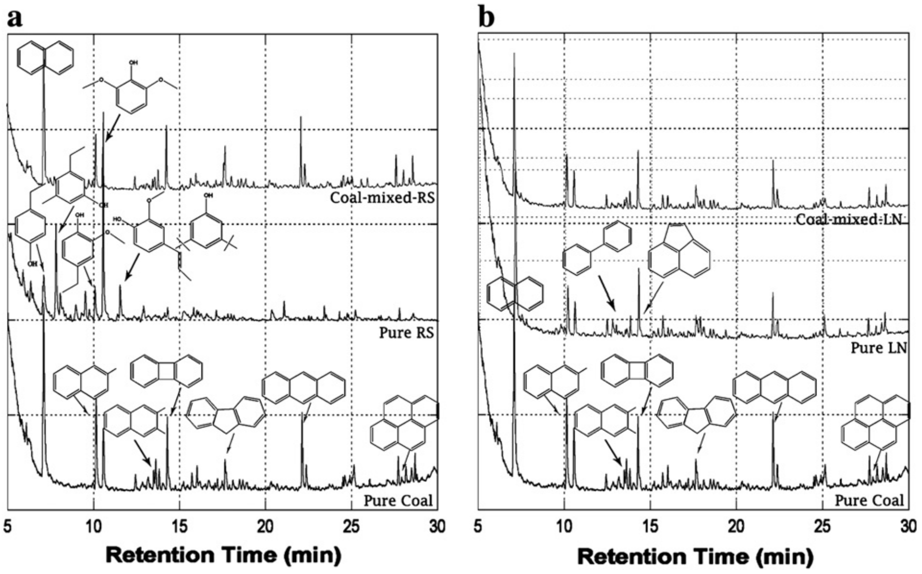


Fig. 5. Chemical structure of the pyrolytic tar, as measured by GC–MS, derived from the pyrolysis at 800 °C of (a) pure coal, pure RS and coal/RS blend with coal and RS ratio of 1:1 (b) pure coal, pure LN and coal/LN blend with coal and LN ratio of 1:1.

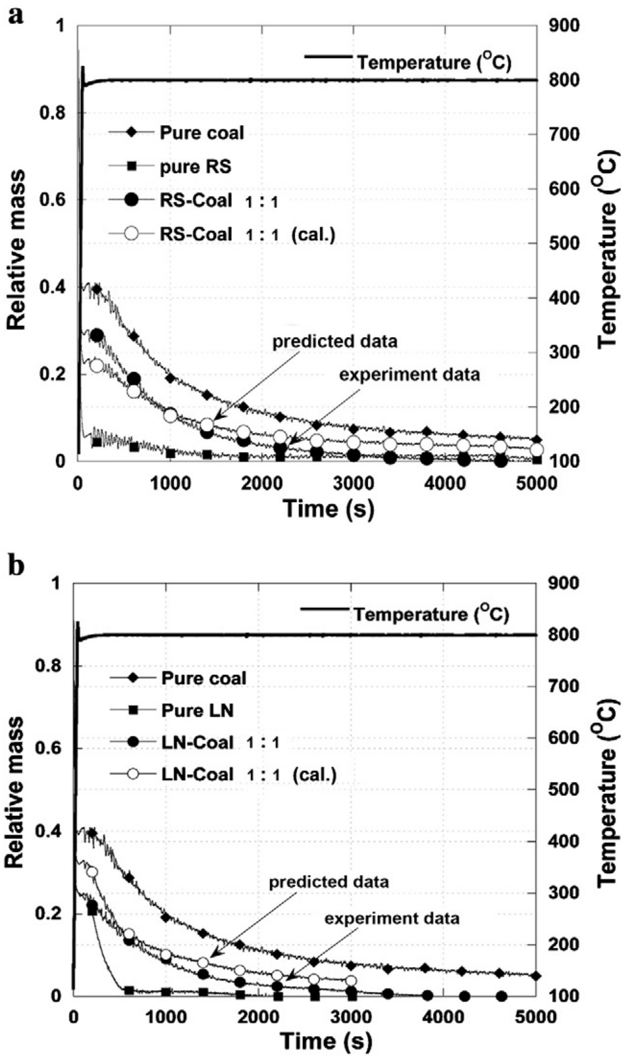


Fig. 6. Relative mass loss of the *in situ* char over time during steam gasification in a thermobalance reactor. Shown is that for char from (a) coal, RS and coal/RS blend with coal and RS ratio of 1:1, and (b) coal, LN and coal/LN blend with coal and LN ratio of 1:1.

expected. However, the synergy in terms of char gasification rate was not observed in the previous study although char was prepared from the rapid heating co-pyrolysis of rice straw and bituminous coal with biomass and coal ratio of 1:1 [16]. It was probably due to the relatively high pyrolysis temperature used (1200 °C) leading to loss of the active surfaces and the catalytic K species on the obtained char. Therefore, the obvious synergetic effect in terms of char steam gasification rate, which was reported here, was not only described by the rapid heating during char preparation but also the development of char structure and the high amount of K retained in the chars. They are the essential factors to promote the gasification of char with steam. Comparing the two types of biomass, the magnitude of the difference between the experimental and the predicted *k* values was larger for the coal/RS blend than for the coal/LN blend (Table 3). This is due to the higher amount of K retained in the char obtained from coal/RS pyrolysis than that of the case of coal/LN blend, as mentioned in Section 3.2. This could explain why the synergetic effect in terms of the char gasification rate with steam of coal/RS blend was more dominant than that of coal/LN blend.

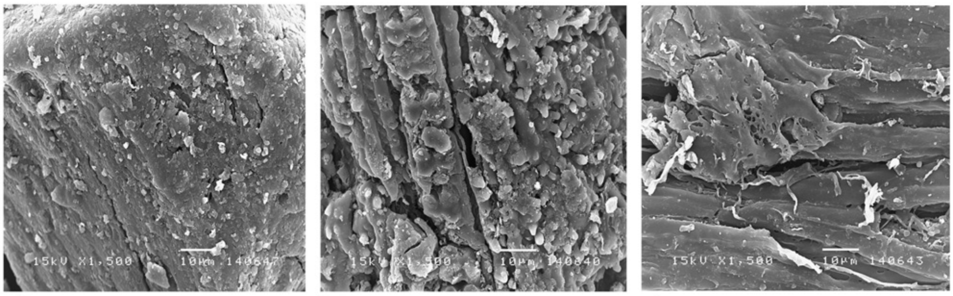
3.4. Characterization of char and tar from co-pyrolysis

The residual char after pyrolysis was characterized by SEM and BET analysis. In the SEM images the coal char appeared to have a smooth surface of dense hydrocarbon molecules with small pores, while the biomass char had a more porous structure with larger pores (Fig. 7). This was attributed to the higher volatile matter content in the biomass (Table 1). In the chars derived from coal/biomass blend, the morphology clearly changed from that seen with coal char into a loose packed and more porous structure (Fig. 7e and g). These changes are likely relevant

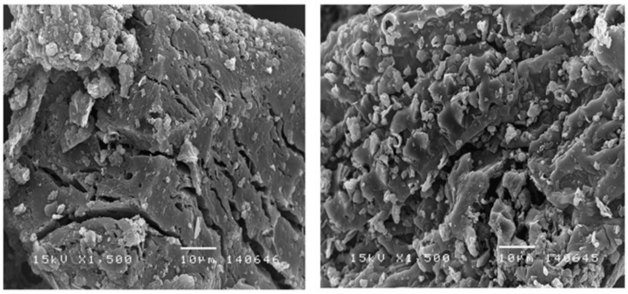
Table 3
Overall rate constant (*k*) of char steam gasification in cases of coal and biomass blends.

Overall rate constant[a] ($\times 10^{-3}$ s^{-1})	RS:coal = 1:1 (w/w)	LN:coal = 1:1 (w/w)
Experimental value	1.031 ($R^2 = 0.99$)	1.112 ($R^2 = 0.95$)
Predicted value[b]	0.442 ($R^2 = 0.91$)	0.805 ($R^2 = 0.95$)

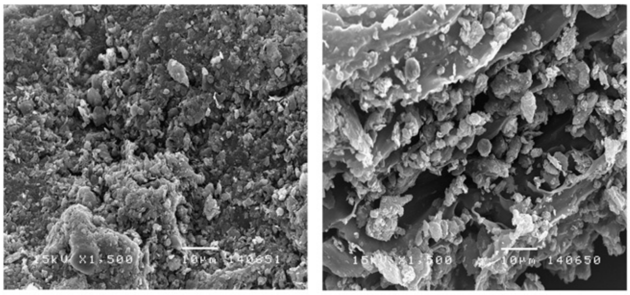
[a] The overall rate constant followed the first-order kinetic rate equation.
[b] Calculate from the data of pure coal and pure biomass.



a) pure coal char **b)** pure RS char **c)** pure LN char



d) coal char in coal/RS blend **e)** RS char in coal/RS blend



f) coal char in coal/LN blend **g)** LN char in coal/LN blend

Fig. 7. SEM images (1500× magnification) of chars from the pyrolysis of (a) coal, (b) RS and (c) LN, plus the (d) coal or (e) RS in coal/RS blend with coal and RS ratio of 1:1, and the (f) coal or (g) LN in coal/LN blend with coal and LN ratio of 1:1.

to the increased reactivity of the chars derived from the coal/RS and coal/LN blends, as mentioned in Section 3.3. In addition, BET surface area and pore volume of the chars derived from coal/biomass blend were higher than the predicted values (Table 3). Thus, the change in the BET surface area and pore volume of the chars from the coal/biomass blend was consistent with the change in their morphology, as mentioned above. Interestingly, the char obtained from the coal/RS blend gave a higher BET surface area and pore volume than that from either coal (1.07- and 1.11-fold, respectively) or RS (1.64- and 1.36-fold, respectively) (Table 3), which may explain the higher reactivity of the coal/RS blend char with steam since the surface area and pore volume are important parameters controlling the reactivity of char [27].

The chemical structure of the tar released during pyrolysis at 800 °C was analyzed by GC–MS over the retention time range of 5–30 min. The pyrolytic coal tar mainly contained the aromatic hydrocarbons (1, 2, 3 and 4 rings) and their isomeric structures, such as naphthalene, fluorene, phenanthrene, anthracene, pyrene and fluoranthene (Fig. 5). These structures are poorly decomposed because of the high energy bond of the resonance $-\mathrm{C}{=}\mathrm{C}-$ in their aromatic rings (more than 1000 kJ mol^{-1}). This result agrees with a previous report that the tar derived from coal pyrolysis contained PAHs and high molecular weight aliphatic hydrocarbons (C_{50}) [28]. In this study, high molecular weight aliphatic hydrocarbons could not be observed because their molecular weight is over the limit of the scanning range (m/z) of the MS (max. m/z = 650).

The tar obtained from the pyrolysis of RS was composed of phenolic and oxygenated compounds, such as ketones, aldehydes, carboxylic acid and some aromatic compounds, consistent with the reported composition of oil derived from the fast pyrolysis of biomass [29]. In the coal/RS blend, the tar composition was clearly different from that of both coal and RS. The peaks of phenolic and oxygenated compounds disappeared while the aromatic compounds, such as naphthalene, anthracene and pyrene, were presented instead. Presumably, the oxygenated compounds in the original RS-tar condensed over the coal char to originate oxygenated-coke species. At the same time, the volatile K would preferentially interact with the coke to form the phenolate groups (K–O–C) over the char surface. The phenolate groups have been reported to play a catalytic role in char steam gasification [25,30,31].

The GC–MS pattern of the pyrolytic tar derived from the coal/LN blend (Fig. 5b), exhibited similar peaks of aromatic compounds to that of the tar derived from coal and LN. Nevertheless, the peak intensity was lower in the coal/LN blend. With respect to the mechanism of heavy tar decomposition over an alumina bed, it has been reported that nascent tar was first decomposed to form coke over acidic alumina sites and then the coke acted as a catalyst for heavy tar decomposition by the accompanying AAEM species [32]. Accordingly, in the pyrolysis of the coal/LN blend here, it is assumed that the porous structure of the coal char might promote the condensation of nascent tar, forming coke over the coal char particles [33]. Consequently, the volatile K from LN would have been deposited, leading to the formation of catalytic sites for heavy tar decomposition. If so, this would provide a potential reason for why the coal/LN blend tar yield was significantly decreased (Section 3.2).

4. Conclusions

Co-pyrolysis of coal and biomass (RS or LN) was performed in a drop tube fixed-bed reactor and the effects of the biomass and coal blending ratio and biomass type on the product distribution, gas composition and product characteristics were investigated. A synergetic effect between coal and the biomass, in terms of higher gas and lower tar and char yields, was observed under this experiment, especially at biomass and coal blending ratio of 1:1 (w/w). This synergetic effect could be attributed to the OH and H radicals formed from the biomass pyrolysis transferring to the coal structure resulting in improving the decomposition of coal. Secondary char formation was also suppressed by the H-transferring behavior in the coal/biomass blends. In addition, the potential catalytic effect of AAEM species in biomass, especially K, appeared to be a potentially significant parameter affecting the observed synergy during the coal/biomass co-pyrolysis.

The gasification reactivity of *in situ* formed char with steam was also examined in a rapid heating thermobalance reactor. Synergetic effect in terms of the weight decrease of the char and the overall rate constant (k) was observed from the coal/biomass blend. Finally, it was found that the biomass type, RS or LN, influenced the magnitude of the synergetic effect during co-pyrolysis. Oxygenated tar released from RS potentially induced volatile-K to form phenolate groups on the char enhancing the char reactivity in steam gasification. On the other hand, aromatic or heavy tar produced from the pyrolysis of LN was likely to promote the deposition of K on the char which then played a catalytic role in the decomposition of the heavy tar itself.

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